

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
REQUEST FOR FILING NATIONAL PHASE OF
PCT APPLICATION UNDER 35 U.S.C. 371 AND 37 CFR 1.494 OR 1.495

Hon. Commissioner of Patents
Washington, D.C. 20231



00909

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)

Atty Dkt: P 282717 /SMC60340/UST
M# /Client Ref.

From: Pillsbury Winthrop LLP, IP Group:

Date: August 1, 2001

This is a **REQUEST** for **FILING** a PCT/USA National Phase Application based on:

| | | |
|---|--|--|
| 1. International Application <u>PCT/GB00/00060</u> ↑ country code | 2. International Filing Date <u>12 JAN 2000</u> Day MONTH Year | 3. Earliest Priority Date Claimed <u>04 FEB 1999</u> Day MONTH Year (use item 2 if no earlier priority) |
|---|--|--|

Measured from the earliest priority date in item 3, this PCT/USA National Phase Application Request is being filed within:

(a) ☐ 20 months from above item 3 date (b) ☒ 30 months from above item 3 date,

(c) Therefore, the due date (unextendable) is August 4, 2001

Title of Invention PRINTING INKS

Inventor(s) ROTHWELL, Geoffrey et al

Applicant herewith submits the following under 35 U.S.C. 371 to effect filing:

☒ Please immediately start national examination procedures (35 U.S.C. 371 (f)).

8. ☒ **A copy of the International Application** as filed (35 U.S.C. 371(c)(2)) is transmitted herewith (file if in English but, if in foreign language, file only if not transmitted to PTO by the International Bureau) including:

- a. ☒ Request;
- b. ☒ Abstract;
- c. 13 pgs. Spec. and Claims;
- d. 0 sheet(s) Drawing which are ☐ informal ☐ formal of size ☐ A4 ☐ 11"

9. ☒ **A copy of the International Application has been transmitted by the International Bureau.**

10. **A translation of the International Application** into English (35 U.S.C. 371(c)(2))

- a. ☐ is transmitted herewith including: (1) ☐ Request; (2) ☐ Abstract;
(3) _____ pgs. Spec. and Claims;
(4) _____ sheet(s) Drawing which are: ☐ informal ☐ formal of size ☐ A4 ☐ 11"
- b. ☐ is not required, as the application was filed in English.
- c. ☐ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.
- d. ☐ Translation verification attached (not required now).

RE: USA National Phase Filing of PCT /GB00/00060

09/890457

11. ☒ Please see the attached Preliminary Amendment
12. ☐ Amendments to the claims of the International Application **under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., before 18th month from first priority date above in item 3, are transmitted herewith (file only if in English) including:**
13. ☒ PCT Article 19 claim amendments (if any) have been transmitted by the International Bureau
14. ☐ Translation of the amendments to the claims **under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., of claim amendments made before 18th month, is attached (required by 20th month from the date in item 3 if box 4(a) above is X'd, or 30th month if box 4(b) is X'd, or else amendments will be considered canceled).**

15. **A declaration of the inventor (35 U.S.C. 371(c)(4))**
- a. ☐ is submitted herewith ☐ Original ☐ Facsimile/Copy
- b. ☒ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.

16. **An International Search Report (ISR):**

- a. Was prepared by ☒ European Patent Office ☐ Japanese Patent Office ☐ Other
- b. ☒ has been transmitted by the international Bureau to PTO.
- c. ☒ copy herewith (2 pg(s).) ☒ plus Annex of family members (1 pg(s).).

International Preliminary Examination Report (IPER):

- a. ☒ has been transmitted (if this letter is filed after 28 months from date in item 3) in English by the International Bureau with Annexes (if any) in original language.
- b. ☒ copy herewith in English.
- c.1 ☒ IPER Annex(es) in original language ("Annexes" are amendments made to claims/spec/drawings during Examination) including attached amended:
- c.2 ☐ Specification/claim pages # _____ claims # 1 - 16
Dwg Sheets # _____
- d. ☐ Translation of Annex(es) to IPER **(required by 30th month due date, or else annexed amendments will be considered canceled).**

Information Disclosure Statement including:

- a. ☒ Attached Form PTO-1449 listing documents
- b. ☒ Attached copies of documents listed on Form PTO-1449
- c. ☒ A concise explanation of relevance of ISR references is given in the ISR.

19. ☐ **Assignment** document and Cover Sheet for recording are attached. Please mail the recorded assignment document back to the person whose signature, name and address appear at the end of this letter.
20. ☐ Copy of Power to IA agent.
21. ☐ **Drawings** (complete only if 8d or 10a(4) not completed): ____ sheet(s) per set: ☐ 1 set informal;
☐ Formal of size ☐ A4 ☐ 11"

22. Small Entity Status ☒ is **Not** claimed ☐ is claimed (pre-filing confirmation required)
- 22(a) _____ (No.) Small Entity Statement(s) enclosed (since 9/8/00 Small Entity Statements(s) not essential to make claim)

23. **Priority** is hereby claimed under 35 U.S.C. 119/365 based on the priority claim and the certified copy, both filed in the International Application during the international stage based on the filing in (country) Great Britain of:

| | <u>Application No.</u> | <u>Filing Date</u> | | <u>Application No.</u> | <u>Filing Date</u> |
|-----|------------------------|--------------------|-----|------------------------|--------------------|
| (1) | 9902386.3 | 04 FEB 1999 | (2) | _____ | _____ |
| (3) | _____ | _____ | (4) | _____ | _____ |
| (5) | _____ | _____ | (6) | _____ | _____ |

- a. ☒ See Form PCT/IB/304 sent to US/DO with copy of priority documents. If copy has not been received, please proceed promptly to obtain same from the IB.
- b. ☐ Copy of Form PCT/IB/304 attached.

RE: USA National Phase Filing of PCT/ /

09/890457

24. Attached:

25 Per Item 17.c2, **cancel original** pages #_____, claims #_____, Drawing Sheets #

26. Calculation of the U.S. National Fee (35 U.S.C. 371 (c)(1)) and other fees is as follows:

Based on amended claim(s) per above item(s) ☐ 12, ☐ 14, ☐ 17, ☐ 25 (hilit)

| | | | | |
|--|------------|-------------------|-----|---------|
| Total Effective Claims | minus 20 = | x \$18/\$9 = | \$0 | 966/967 |
| Independent Claims | minus 3 = | x \$80/\$40 = | \$0 | 964/965 |
| If any proper (ignore improper) Multiple Dependent claim is present, | | add \$270/\$135 + | 0 | 968/969 |

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(4)): →→ **BASIC FEE REQUIRED, NOW** →→→→

A. If country code letters in item 1 are not "US", "BR", "BB", "TT", "MX", "IL", "NZ", "IN" or "ZA"

See item 16 re:

| | | | |
|--|------------------|------|---------|
| 1. Search Report was <u>not</u> prepared by EPO or JPO ----- | add \$1000/\$500 | | 960/961 |
| 2. Search Report was prepared by EPO or JPO ----- | add \$860/\$430 | +860 | 970/971 |

SKIP B, C, D AND E UNLESS country code letters in item 1 are "US", "BR", "BB", "TT", "MX", "IL", "NZ", "IN" or "ZA"

| | | | |
|---|------------------|----|---------|
| → <input type="checkbox"/> B. If <u>USPTO</u> did not issue <u>both</u> International Search Report (ISR) <u>and</u> (if box 4(b) above is X'd) the International Examination Report (IPER), ----- | add \$1000/\$500 | +0 | 960/961 |
| → <input type="checkbox"/> C. If <u>USPTO</u> issued ISR but not IPER (or box 4(a) above is X'd), ----- | add \$710/\$355 | +0 | 958/959 |
| → <input type="checkbox"/> D. If <u>USPTO</u> issued IPER but IPER Sec. V boxes <u>not all</u> 3 YES, ----- | add \$690/\$345 | +0 | 956/957 |
| → <input type="checkbox"/> E. If international preliminary examination fee was paid to <u>USPTO</u> and Rules 492(a)(4) and 496(b) <u>satisfied</u> (IPER Sec. V <u>all</u> 3 boxes YES for <u>all</u> claims), ----- | add \$100/\$50 | +0 | 962/963 |

27. **SUBTOTAL = \$860**

28. If Assignment box 19 above is X'd, add Assignment Recording fee of ---\$40 +0 (581)

29. Attached is a check to cover the ----- **TOTAL FEES \$860**

Our Deposit Account No. 03-3975

Our Order No. 70662 282717
C# M#



00909

CHARGE STATEMENT: The Commissioner is hereby authorized to charge any fee specifically authorized hereafter, or any missing or insufficient fee(s) filed, or asserted to be filed, or which should have been filed herewith or concerning any paper filed hereafter, and which may be required under Rules 16-18 and 492 (missing or insufficient fee only) now or hereafter relative to this application and the resulting Official document under Rule 20, or credit any overpayment, to our Account/Order Nos. shown above for which purpose a duplicate copy of this sheet is attached.

This CHARGE STATEMENT does not authorize charge of the issue fee until/unless an issue fee transmittal form is filed

Pillsbury Winthrop LLP
Intellectual Property Group

By Atty: Paul N. Kokulis

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NOTE: File in duplicate with 2 postcard receipts (PAT-103) & attachments.

JC17 Rec'd PCT/PTO 01 AUG 2001

09/890457

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PATENT APPLICATION OF

Inventor(s): ROTHWELL, G et al

Filed: Herewith

Title: PRINTING INKS

AUGUST 1, 2001

PRELIMINARY AMENDMENT

Hon. Commissioner of Patents
Washington, D.C. 20231

Sir:

Please amend this application as follows:

IN THE SPECIFICATION:

At the top of the first page, just under the title, insert

☒ --This application is the National Phase of International Application
PCT/GB00/00060 filed January 12, 2000 which designated the U.S.

and that International Application

☒ was ☐ was not published under PCT Article 21(2) in English.--

Respectfully submitted,

PILLSBURY WINTHROP LLP
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APPLICANTS

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TITLE

PRINTING INKS

09/890457-12001

PRINTING INKS

The present invention relates to non-aqueous printing inks containing pigments and their use in "drop-on-demand" ink jet printers.

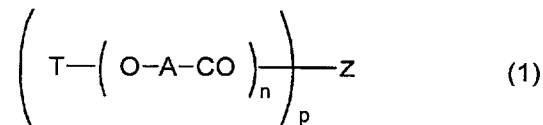
One of the most important class of ink jet printers is the so-called "drop-on-demand" (hereinafter DOD) printer, where droplets of ink are expelled from a print head to make a print mark only when desired to form an image during the printing process. DOD printers use either an electrostatically accelerated ink jet or sequence of droplets which are ejected by pressure impulse actuation. In the latter type of DOD printer, each ink droplet is individually ejected from a nozzle in the print head by means of pressure pulses which are induced, for example, by a piezo-electric actuator acting on the ink in a channel supplying the nozzle or by generation of a vapour bubble in response to a thermal pulse.

One particular problem encountered in continuous printing with ink jet printers is that a small amount of the tail of the droplet being ejected tends to separate from the droplet and collect on that part of the surface of the print head immediately surrounding the nozzle. With high speed printers, there is less opportunity for this tail of the droplet to recede back into the nozzle before the next pressure pulse which results in the build up of an ink residue on the surface of the print head giving a distorted printed mark. This is particularly marked in high dot density printers and especially colour printers. This has led to the introduction of coatings for the print head to reduce the accumulation of such residues but even so the print head still requires cleaning resulting in down-time of the printer.

Improved print performance in DOD printers has been sought by advances in printing ink formulations. Thus, WO 97/15633 discloses a printing ink containing a pigment which is dispersed in a non-aqueous medium using a polyester amine dispersant where some of the basic amine groups in the dispersant are neutralised with an acid or acidic phenolic compound. These printing inks are stated to exhibit a reduction in the amount of residual ink which forms on the print head at the end of each pulse by improving the rate at which the tail of the droplet retreats into the nozzle of the print head. One method of determining the propensity of an ink droplet to retreat back into the nozzle is to measure the Receding Meniscus Velocity (hereinafter RMV) of the printing ink on a surface, such as a fluorosilane coated metal surface. One such method of measuring RMV is described in WO 97/15633.

It has now been found that printing inks exhibiting a superior RMV can be made by dispersing a pigment in a non-aqueous medium by means of a dispersant containing a higher proportion of polyester to those described in WO 97/15633.

According to a first aspect of the present invention there is provided a drop on demand ink jet printing ink comprising a pigment, a substantially non-aqueous medium and a dispersant of Formula (1)



5 wherein

T is hydrogen or a polymerisation terminating group;

A is C₈₋₂₀-linear alkylene or alkenylene;

Z is the residue of a polyamine or polyimine;

n is from 2 to 10;

p is not less than 2; and

the weight ratio of (T-(O-A-CO)_n)_p to Z is from 5:1 to 20:1; including salts thereof.

The dispersant of Formula 1 is hereinafter referred to as The Dispersant.

When T is a polymerisation terminating group, it is preferably the residue of a carboxylic acid of formula T-COOH wherein T is aliphatic which may be linear or branched, saturated or unsaturated but is preferably linear and preferably saturated. The number of carbon atoms in T can be as high as 50. It is preferred that T contains not less than 8, more preferably not less than 12 and especially not less than 14 carbon atoms. It is also preferred that T contains not greater than 30, preferably not greater than 25 and especially not greater than 20 carbon atoms.

Preferably, A contains not less than 10, more preferably not less than 12 and especially not less than 14 carbon atoms.

The integer n is preferably not less than 3 and especially not less than 4. It is also preferred that n is not greater than 8 and especially not greater than 6.

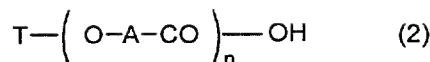
The integer p is preferably not greater than 2000 and especially not greater than 1000.

Z is preferably the residue of polyallylamine, polyvinylamine, more preferably poly(C₂₋₄-alkyleneimine) (hereinafter PAI) and particularly poly(ethyleneimine) (PEI).

The PAI may be linear or more preferably branched.

The polyamine or polyimine preferably has a number-average molecular weight from 500 to 600,000, more preferably from 1,000 to 200,000, even more preferably from 1,000 to 100,000 and especially from 5,000 to 100,000.

The Dispersant is obtainable by reacting the polyamine or polyimine with an end-capped polyoxyalkylenecarbonyl acid or polyoxyalkenylenecarbonyl acid (hereinafter TPOAC acid) of formula 2:



wherein T, A, and n are as defined hereinbefore.

The number-average molecular weight (Mn) of the TPOAC acid is preferably not less than 500 and especially not less than 800. It is also preferred that the number-average molecular weight of the TPOAC acid is not greater than 3000 and especially not greater than 2000.

The weight ratio of $(T-(O-A-CO)_n)_p$ to Z is preferably not less than 7:1, more preferably not less than 8:1 and especially not less than 9:1. It is also preferred that the weight ratio of $(T-(O-A-CO)_n)_p$ to Z is not greater than 17:1, more preferably not greater than 15:1 and especially not greater than 13:1. Particularly useful effects have been obtained when the weight ratio of $(T-(O-A-CO)_n)_p$ to Z is from 10:1 to 15:1 and especially from 10:1 to 13:1.

The salts of The Dispersants may be those of any inorganic or organic acid including quaternary ammonium salts, particularly those obtainable by reacting The Dispersant with a dialkylsulphate such as dimethylsulphate or an alkylhalide such as ethylchloride.

Preferably, the salt of The Dispersant is that obtained with an organic or inorganic acid. Examples of suitable acids are hydrochloric, sulphuric and acetic acids. The salt may also be that of an acidic phenol or phenolic polymer. Preferably, The Dispersant is in the form of its free-base.

Particularly useful effects have been obtained when the TPOAC acid is derived from ricinoleic acid and especially 12-hydroxystearic acid, particularly commercially available material which contains a small amount of stearic acid as impurity which acts as a polymerisation terminating or end-cap group in the preparation of the TPOAC acid.

The Dispersants are made by a similar process to Example 7/Agent H disclosed in GB 2,001,083.

The pigment may be from any of the recognised classes of pigments described, for example, in the Third Edition of the Colour Index (1971) and subsequent revisions of, and supplements thereto, under the chapter heading "Pigments". Examples of inorganic pigments are titanium dioxide, zinc oxide, Prussian blue, cadmium sulphide, iron oxides, vermilion, ultramarine and the chrome pigments, including chromates, molybdates and mixed chromates and sulphates of lead, zinc, barium, calcium and mixtures and modifications thereof which are commercially available as greenish-yellow to red pigments under the names primrose, lemon, middle, orange, scarlet and red chromes. Examples of organic pigments are those from the azo, disazo, condensed azo, thioindigo, indanthrone, isoindanthrone, anthanthrone, anthraquinone, isodibenzanthrone, triphenyldioxazine, quinacridone, perylene, diketopyrrolopyrrole and phthalocyanine series, especially copper

phthalocyanine and its nuclear halogenated derivatives, and also lakes of acid, basic and mordant dyes. Carbon black, although strictly inorganic, behaves more like an organic pigment in its dispersing properties. Preferred organic pigments are phthalocyanines, especially copper phthalocyanines, monoazos, disazos, indanthrones, anthranthrones, quinacridones and carbon blacks.

The printing ink is preferably made by milling the pigment in the non-aqueous medium in the presence of The Dispersant to give a pigment dispersion which is subsequently let down to give the printing ink.

Whereas the non-aqueous may contain up to 2% by weight water it is preferably free from water.

The non-aqueous medium is preferably a substantially non-polar organic liquid.

Substantially non-polar, organic liquids which may be used, either alone or in admixture are aromatic hydrocarbons, such as toluene and xylene, halogenated aliphatic and aromatic hydrocarbons, such as trichloro-ethylene, perchloroethylene and chlorobenzene and particularly aliphatic and aromatic hydrocarbons having at least 6 carbon atoms including mixtures thereof, for example, refinery distillation products and by products.

Preferably, the non-aqueous medium has a polar solubility parameter of not greater than $7.0 \text{ MPa}^{1/2}$ as measured using the method of Hansen, C.M. and Skaarup, K., Journal of Paint Technology, 39 No. 51, 1967, pages 511-514 as described by Patton, T.C. in "Paint Flow and Pigment Dispersion", second edition, Wiley Printerscience, 1979. Examples of non-aqueous media with polar solubility parameters of $7.0 \text{ MPa}^{1/2}$ or less are non-polar organic liquids including mixtures with polar organic liquids wherein the amount of polar liquid is preferably less than 45%, more preferably less than 30%, even more preferably less than 20% and especially less than 10% by weight based upon the weight of the mixture of non-polar and polar organic liquids.

It is especially preferred that the non-aqueous medium with a polar solubility parameter not greater than $7.0 \text{ MPa}^{1/2}$ is an aliphatic hydrocarbon such as those commercially available as Exxsol, Solvesso, Exxon naphtha, Isopar, Pegasol, Lytol and Shellsol.

Particularly suitable non-aqueous media are mixtures of an aliphatic hydrocarbon and a C_{10-30} -aliphatic fatty alcohol which may be linear or branched, saturated or unsaturated. Examples of suitable alcohols are stearyl, lauryl and especially oleyl alcohol.

The dispersion of the pigment in the substantially non-aqueous medium may contain other ingredients which are commonly used in the printing ink industry such as binders, fluidising agents such as those described in GB-A-1508576 and GB-A-2108143, antisedimentation agents, levelling agents and preservatives.

Preferably the ink contains from 2 to 20%, more preferably from 4 to 15% pigment based upon the weight of the ink.

As noted hereinbefore, it is preferable to prepare a concentrated dispersion of the pigment which is subsequently diluted to form the final printing ink.

5 The dispersions typically contain from 5 to 95% by weight of the pigment, the precise quantity depending on the nature of the pigment and the quantity depending on the nature of the pigment and the relative densities of the pigment and the non-aqueous medium. For example, a dispersion which contains an organic pigment, preferably contains from 15 to 60% by weight of the solid whereas a dispersion in which the solid is
10 an inorganic pigment, preferably contains from 40 to 90% by weight of the pigment based on the total weight of dispersion.

The amount of The Dispersion is preferably from 10 to 100%, more preferably from 10% to 70% and especially from 20% to 50% based on the amount of pigment.

15 The dispersion may be obtained by any of the conventional methods known for preparing dispersions. Thus, the pigment, the non-aqueous medium and The Dispersant may be mixed in any order, the mixture then being subjected to a mechanical treatment to reduce the particles of the pigment to an appropriate size, for example by ball milling, bead milling, gravel milling or plastic milling until the dispersion is formed. Alternatively, the solid may be treated to reduce its particle size independently or in admixture with either
20 the non-aqueous medium or the dispersant, the other ingredient or ingredients then being added and the mixture being agitated to provide the dispersion.

If a composition containing pigment and The Dispersant is required in dry form, the non-aqueous medium is preferably volatile so that it may be readily removed from the particulate pigment by a simple separation means such as evaporation. It is preferred,
25 however, that the composition is a dispersion.

If the dry composition consists essentially of The Dispersant and a pigment, it preferably contains at least 0.2%, more preferably at least 0.5% and especially at least 1.0% dispersant based on weight of the pigment. Preferably the dry composition contains not greater than 100%, preferably not greater than 50%, more preferably not greater than
30 20% and especially not greater than 10% by weight based on the weight of the pigment.

35 The printing ink may additionally contain an RMV modifier which may be a Lewis acid, an organic or inorganic acid or a phenolic compound. Examples of RMV modifiers are acetic, citric, tartaric, toluic and p-naphthoic acids, naphthalene-2-sulphonic acid and p-toluene sulphonic acid; resorcinol and 2-naphthol; alkyl partial esters of phosphorus acids and linear phenolic polymers such as novolak resins. The preferred RMV modifier is a novolak resin, especially those containing a 4-alkyl substituent and particularly those with a C₁₋₁₀- and especially a C₄₋₈-alkyl group. Useful effects have been obtained with Uravar FN5 as RMV modifier.

The most suitable RMV for any given printing ink can be readily determined using the protocol described in WO 97/15633 which protocol may also be used to establish the optimum amount of RMV modifier. The amount of RMV modifier in the ink is generally not greater than 10%, preferably not greater than 5% and especially not greater than 2%.

In view of the foregoing preferences an especially preferred printing ink according to the first aspect of the invention comprises a pigment, a dispersant of the Formula (1), a substantially non-aqueous medium and a RMV modifier as hereinbefore defined.

The printing inks according to the first aspect of the present invention preferably have a viscosity at 25°C of less than 50cP, more preferably less than 20cP, especially less than 15cP and more especially from 7 to 15cP.

According to a second aspect of the present invention there is provided a process for printing an image on a substrate comprising applying thereto by means of a drop on demand ink jet printer a printing ink according to the first aspect of the invention.

The preferred inks used in this process are the preferred inks hereinbefore described in relation to the first aspect of the present invention.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a piezoelectric crystal causes ejection of the ink from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, plastic, an overhead projector slide or a textile material.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Examples of commercially available papers include, HP Premium Coated Paper, HP Photopaper (all available from Hewlett Packard Inc), Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film, Epson Photo Quality Glossy Paper (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper, Canon GP 201 Glossy Paper, Canon HG 101 High Gloss Film (all available from Canon Inc.), Wiggins Conqueror paper (available from Wiggins Teape Ltd), Xerox Acid Paper and Xerox Alkaline paper.

Preferred textile materials are natural, synthetic and semi-synthetic materials. Examples of preferred natural textile materials include wool, silk, hair and cellulosic materials, particularly cotton, jute, hemp, flax and linen. Examples of preferred synthetic and semi-synthetic materials include polyamides, polyesters, polyacrylonitriles and polyurethanes.

A third aspect of the present invention provides a substrate printed with an ink according to the first aspect of the present invention, or by means of the process according to the second aspect of the present invention.

A fourth aspect of the present invention provides an ink jet printer cartridge containing an ink according to the first aspect of the present invention.

The invention is further illustrated by the following examples where all references to amounts are in parts by weight unless indicated to the contrary.

Examples 1 to 3 and Comparative Example A: Black Inks

Millbases were prepared having the composition outlined in Table 1 below by milling the components as indicated in the presence of glass beads (3mm, 125 parts) on a horizontal Red Devil shaker for 90 minutes. After milling, the beads were removed and the millbase diluted with oleyl alcohol (7.1 parts, Novol ex Croda Chemicals) and an aliphatic hydrocarbon mineral oil (28.4 parts, Lytol ex Witco) to give a printing ink.

The Receding Meniscus Velocity of the inks (RMV) was measured at 30°C using the method described in WO 97/15633. The results are given in Table 2 below which clearly show that the dispersants according to the present invention (Dispersants (1), (2) and (3)) provide inks which exhibit a superior (higher) RMV compared to Dispersant A (a comparative dispersant which has a weight ratio of $(T-(O-A-CO)_n)_p$ to Z is 3.5:1 and therefore outside the scope of the present invention).

Table 1

| Example | 1 | 2 | 3 | A |
|-----------------------------------|--------------|--------------|--------------|--------------|
| Millbase | 1 | 2 | 3 | 4 |
| Regal 250R (pigment) | 5.00 | 5.00 | 5.00 | 5.00 |
| Dispersant 1 | 1.37 | - | - | - |
| Dispersant 2 | - | 1.37 | - | - |
| Dispersant 3 | - | - | 1.37 | - |
| Dispersant A | - | - | - | 1.71 |
| Solsperse 5000 (fluidising agent) | 0.09 | 0.09 | 0.09 | 0.09 |
| Hydrocarbon solvent | 3.54 | 3.54 | 3.54 | 3.20 |
| | 10.00 | 10.00 | 10.00 | 10.00 |

Footnote to Table 1

Regal 250R is carbon black pigment ex Cabot Corporation

Dispersant 1 is a 50% solution of PHS/PEI (7:1) in Lytol

Dispersant 2 is a 50% solution of PHS/PEI (10:1) in Lytol

Dispersant 3 is a 50% solution of PHS/PEI (13:1) in Lytol

Dispersant A is a 40% solution of PHS/PEI (3.5:1) in Lytol

Solsperse 5000 is a quaternary ammonium salt of sulphonated copper phthalocyanine ex Zeneca Ltd.

Hydrocarbon solvent is Lytol ex Witco.

Dispersant A is made by the process described in Example 7/Agent H in GB 2 001 083.

Dispersants 1 to 3 are made by a similar process to that described for Dispersant A except that the ratio of poly(12-hydroxystearic acid) to polyethyleneimine (PHS/PEI) is as indicated in parenthesis.

Table 2

| Millbase | Dispersant | RMV (mm/sec at 30°C) |
|----------|------------|-------------------------|
| 1 | 1 | 8.9 |
| 2 | 2 | 10.0 |
| 3 | 3 | 8.7 |
| 4 | A | 7.9 |

Footnote to Table 2

Dispersants 1-3 and A are as hereinbefore described in the footnote to Table 1.

Examples 4 to 6 and Comparative Example B: Red Inks

Millbases were prepared containing a red pigment by a similar method to that described in Examples 1 to 3 by milling together the components listed in Table 3 below. These millbases were then diluted by adding aliphatic hydrocarbon solvent (27.0 parts, Lytol ex Witco). The RMV was again measured using the method described in WO 97/15633. The results are given in Table 4 and show that those inks prepared using dispersants with a higher PHS to PEI ratio exhibit superior RMV to inks prepared using Dispersant A.

Table 3

| Example | 4 | 5 | 6 | B |
|---------------------|-------------|-------------|-------------|-------------|
| Millbase | 5 | 6 | 7 | 8 |
| Hostaperm Red E5B02 | 3.33 | 3.33 | 3.33 | 3.33 |
| Dispersant 1 | 2.34 | - | - | - |
| Dispersant 2 | - | 2.34 | - | - |
| Dispersant 3 | - | - | 2.34 | - |
| Dispersant A | - | - | - | 2.92 |
| Hydrocarbon solvent | 4.33 | 4.33 | 4.33 | 3.75 |
| | 10.0 | 10.0 | 10.0 | 10.0 |

Footnote to Table 3

Hostaperm Red E5B02 is a red pigment ex Hoechst.

Dispersants 1 to 3, dispersant A and hydrocarbon solvent are as explained in the footnote to Table 1.

Table 4

| Millbase | Dispersant | RMV (mm/sec at 30°C) |
|-----------------|-------------------|---------------------------------|
| 5 | 1 | 2.7 |
| 6 | 2 | 2.9 |
| 7 | 3 | 4.6 |
| 8 | A | <1 |

Footnote to Table 4

Dispersants 1 to 3 and A are as hereinbefore described in the footnote to Table 1.

Example 7 and Comparative Example C: Blue Inks

A blue millbase was prepared by milling together the components listed in Table 5 below in a glass vial in the presence of 3mm glass beads (40 parts) for 4 hours on a Red Devil horizontal shaker.

| | Example 4 | Comparative Example C |
|---------------------|-----------|-----------------------|
| Blue Pigment | 3 | 3 |
| Dispersant A | - | 3 |
| Dispersant 2 | 2.4 | - |
| Solsperse 5000 | 0.3 | 0.3 |
| Hydrocarbon Solvent | 4.3 | 3.7 |

Footnote to Table 5

The Blue Pigment is Irgalite Blue GLVO ex Ciba-Geigy.

Dispersants A and 2 and Hydrocarbon Solvent are as explained in the footnote to Table 1.

The glass beads were then removed from the millbase which was let down by adding oleyl alcohol (13.3 parts, Novol ex Croda Chemicals) and hydrocarbon solvent (36.8 parts, Lytol ex Witco) to give a printing ink.

The RMV of each ink was determined using the method described in WO 97/15633. The ink prepared from the millbase of Example 4 exhibited an RMV of 5.9 compared with an RMV of 3.4 for the ink prepared from the millbase of Comparative Example C.

Example 8 and Comparative Example D: Blue Inks

A novolak resin (1 parts of 10% w/w solution of Uravar FN-5 in Lytol) was added to the printing ink prepared as described in Example 7 and Comparative Example C (10 parts) with RMV again measured. These are inks of Example 8 and Comparative Example D, respectively which exhibited RMV of 10.3 and 7.9, respectively. Again, the ink prepared using Dispersant 2 exhibited superior RMV to that prepared using Dispersant A.

Example 9 and Comparative Example E: Yellow Inks

Millbases were prepared in a similar manner to that described in Example 7 and Comparative Example C except using the components and amounts listed in Table 6 below.

Table 6

| | Example 9 | Comparative Example E |
|---------------------|-----------|-----------------------|
| Yellow Pigment | 3 | 3 |
| Dispersant A | - | 3 |
| Dispersant 2 | 2.4 | - |
| Hydrocarbon Solvent | 4.6 | 4 |

Footnote to Table 6

The yellow pigment is Paliotol Yellow D1155 ex BASF Dispersants 2 and A and Hydrocarbon Solvent are as explained in the footnote to Table 1.

A printing ink was prepared by removing the beads and diluting with a letdown consisting of oleyl alcohol (10.8 parts) and hydrocarbon solvent (39.1 parts Lytol). The RMV of the ink prepared from the millbase of Example 9 was 10.2 and that prepared from the millbase of Comparative Example E was 9.3.

Example 10 and Comparative Example F: Yellow Inks

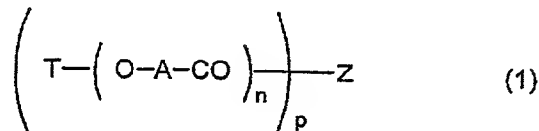
Novolak resin (1.25 parts of 10%w/w solution of Uravar FN-5 in Lytol) was added to the inks of Example 9 and Comparative Example E respectively to give inks of Example 10 and F. The RMV of the ink of Example 10 was 13.2 compared with 12.2 for the ink of Comparative Example F.

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ART 34 AND

CLAIMS

1. A drop on demand ink jet printing ink comprising a pigment, a substantially non-aqueous medium and a dispersant of formula 1



wherein

T is hydrogen or a polymerisation terminating group;

A is C₈₋₂₀-linear alkylene;

Z is the residue of a polyamine or polyimine wherein the number-average molecular weight is from 5,000 to 100,000;

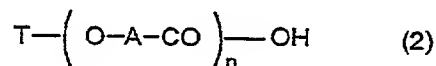
n is from 2 to 10;

p is not less than 2; and

the weight ratio of (T-(O-A-CO)_n)_p to Z is from 5:1 to 20:1.

2. A printing ink as claimed in claim 1 wherein the weight ratio of (T-(O-A-CO)_n)_p to Z is from 9:1 to 13:1.

3. A printing ink as claimed in either claim 1 or claim 2 wherein the dispersant is obtainable by reacting the polyamine or polyimine with an end-capped polyoxyalkylenecarbonyl acid or polyoxyalkenylenecarbonyl acid (TPOAC acid) of formula 2:



wherein T, A and n are as defined in claim 1.

4. A printing ink as claimed in claim 3 wherein the TPOAC acid is derived from 12-hydroxystearic acid.

5. A printing ink as claimed in either claim 3 or claim 4 wherein the number-average molecular weight of the TPOAC acid is from 800 to 2000.

6. A printing ink as claimed in any one of the preceding claims wherein Z is the residue of polyethyleneimine.

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7. A printing ink as claimed in any one of claims 1 to 6 wherein the non-aqueous medium is an aromatic or aliphatic hydrocarbon or mixtures thereof.
8. A printing ink as claimed in claim 7 which additionally comprises a C₁₀₋₃₀-aliphatic fatty alcohol.
9. A printing ink as claimed in any one of claims 1 to 8 wherein the non-aqueous medium has a solubility parameter of 7.0 MPa^{1/2} or less.
10. A printing ink as claimed in any one of claims 1 to 9 which additionally comprises a fluidising agent.
11. A printing ink as claimed in any one of claims 1 to 10 which additionally comprises a Receding Meniscus Velocity (RMV) modifier.
12. A printing ink as claimed in claim 11 where the RMV modifier is a linear phenolic polymer.
13. A printing ink according to any one of the preceding claims wherein the ink has a viscosity at 25°C of less than 50cP.
14. A process for printing an image on a substrate comprising applying thereto by means of a drop on demand ink jet printer a printing ink according to any one of the preceding claims.
15. A substrate printed with an ink according to any one of claims 1 to 13, or by means of the process according to claim 14.
16. An ink jet printer cartridge containing an ink according to any one of claims 1 to 13.

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RULE 63 (37 C.F.R. 1.63)
DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION IN THE
UNITED STATES PATENT AND TRADEMARK OFFICE

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name and I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the INVENTION ENTITLED:

Printing Inks

the specification of which

is attached hereto
 was filed on as U.S. application serial No.
 was filed as PCT international application No. PCT/GB00/00060 on 12/01/2000
 and (if applicable) was amended on

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose all information which is known to me to be material to patentability as defined in 37 C.F.R. 1.56. I hereby claim foreign priority benefits under 35 U.S.C. 119/365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate filed by me or my assignee disclosing the subject matter claimed in this application and having a filing date (1) before that of the application on which priority is claimed, or (2) if no priority is claimed, before the filing date of this application:

PRIOR FOREIGN APPLICATION(S)

| <u>Number</u> | <u>Country</u> | <u>Day/MONTH/Year Filed</u> | <u>Date First Laid</u> <u>Open or published</u> | <u>Date Patented</u> <u>or Granted</u> | <u>Priority claimed</u> <u>Yes No</u> |
|---------------|----------------|-----------------------------|--|---|---|
| 9902386.3 | United Kingdom | 04/02/1999 | | | X |

I hereby claim the benefit under 35 U.S.C. 120/365 of all United States applications listed below and PCT international applications listed above or below and, if this is a continuation-

Status

(patented, pending abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint Pillsbury Winthrop LLP, 1600 Tysons Boulevard, McLean, Virginia 22102, USA, telephone number 861-3000 (to whom all communications should be directed), and the below named persons (of the same address) individually and collectively my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent and I hereby authorise them to act and reply on instructions from and communicate directly with the person/assignee/attorney/firm/organisation who/which first sends/sent this case to them and by who/which I hereby declare that I have consented after full disclosure to be represented unless/until I instruct Pillsbury Winthrop in writing to the contrary.

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17519

Edward M Prince

22429

G Lloyd Knight

17698

James D. Berquist

34776

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18781

David W Brinkman

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Edgar H Martin

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